

Crystal structure of dicesium hydrogen citrate from laboratory single-crystal and powder X-ray diffraction data and DFT comparison

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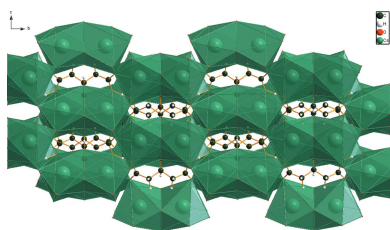
The crystal structure of dicesium hydrogen citrate, $2\text{Cs}^+\cdot\text{C}_6\text{H}_6\text{O}_7^{2-}$, has been solved using laboratory X-ray single-crystal diffraction data, refined using laboratory powder X-ray data, and optimized using density functional techniques. The Cs^+ cation is nine-coordinate, with a bond-valence sum of 0.92 valence units. The CsO_9 coordination polyhedra share edges and corners to form a three-dimensional framework. The citrate anion is located on a mirror plane. Its central hydroxy/carboxylate $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond is short, and (unusually) intermolecular. The centrosymmetric end-end carboxylate hydrogen bond is exceptionally short ($\text{O}\cdots\text{O} = 2.416 \text{ \AA}$) and strong. These hydrogen bonds contribute 16.5 and 21.7 kcal mol^{-1} , respectively, to the crystal energy. The hydrophobic methylene groups occupy pockets in the framework.

1. Chemical context

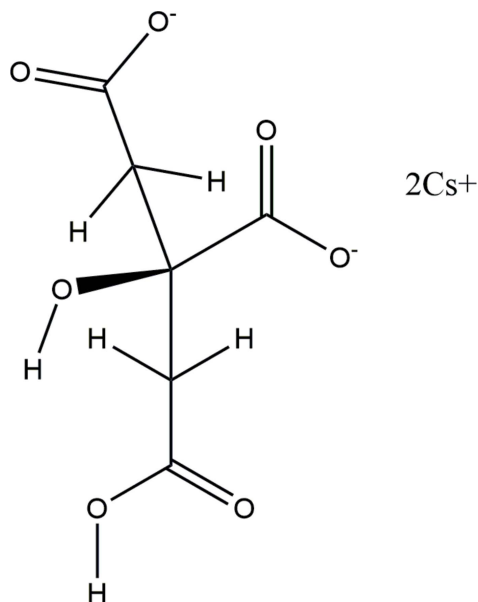
In the course of a systematic study of the crystal structures of group 1 (alkali metal) citrate salts to understand the anion's conformational flexibility, ionization, coordination tendencies, and hydrogen bonding, we have determined several new crystal structures. Most of the new structures were solved using X-ray powder diffraction data (laboratory and/or synchrotron), but single crystals were used where available. The general trends and conclusions about the sixteen new compounds and twelve previously determined structures are being reported separately (Rammohan & Kaduk, 2017a). Eleven of the new structures – $\text{NaKHC}_6\text{H}_5\text{O}_7$, $\text{NaK}_2\text{C}_6\text{H}_5\text{O}_7$, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, $\text{NaH}_2\text{C}_6\text{H}_5\text{O}_7$, $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$, $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$, $\text{Rb}_2\text{HC}_6\text{H}_5\text{O}_7$, $\text{Rb}_3\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$, $\text{Rb}_3\text{C}_6\text{H}_5\text{O}_7$, $\text{Na}_5\text{H}(\text{C}_6\text{H}_5\text{O}_7)_2$, and $\text{CsH}_2\text{C}_6\text{H}_5\text{O}_7$ – have been published recently (Rammohan & Kaduk, 2016a,b,c,d,e, 2017b,c,d,e,f, Rammohan *et al.*, 2016), and two additional structures – $\text{KH}_2\text{C}_6\text{H}_5\text{O}_7$ and $\text{KH}_2\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})_2$ – have been communicated to the Cambridge Structural Database (CSD) (Kaduk & Stern, 2016a,b). We report here synthesis and crystal structure of another alkali metal citrate salt, $2\text{Cs}^+\cdot\text{HC}_6\text{H}_5\text{O}_7^{2-}$.

2. Structural commentary

The asymmetric unit of the title compound is shown in Fig. 1. The root-mean-square deviation of the non-hydrogen atoms in the experimentally determined and in the DFT-optimized structures is 0.098 Å (Fig. 2). The largest differences are 0.13 Å, at Cs19 and O11. This good agreement provides strong



evidence that the experimentally determined structure is correct (van de Streek & Neumann, 2014). The following discussion uses the DFT-optimized structure.



Most of the bond lengths, bond angles, and torsion angles fall within the normal ranges indicated by a *Mercury* Mogul geometry check (Macrae *et al.*, 2008). The C1–C2–C3 angle of 114.1° is flagged as unusual (average = 104.0 (32), Z-score = 3.1). The Cs⁺ cation is 9-coordinate, with a bond-valence sum of 0.92 valence units. The location of the citrate anion on a mirror plane and the coordination of all seven oxygen atoms to Cs⁺ cations presumably are the source of the slight distortion. The citrate anion occurs in the *trans,trans* conformation,

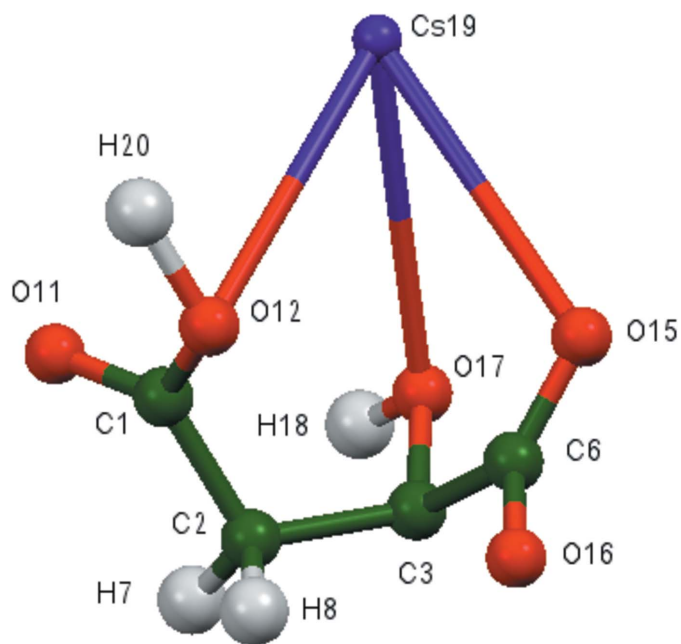


Figure 1
The asymmetric unit of the title compound, with the atom numbering. The atoms are represented by 50% probability spheroids.

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O12–H20···O12 ⁱ	1.208	1.208	2.416	180.0
O17–H18···O16 ⁱⁱ	0.999	1.634	2.632	178.2

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$.

which is one of the two low-energy conformations of an isolated citrate moiety. The citrate anion triply chelates to two Cs⁺ cations through O12, O17, and O15. The citrate also chelates through O12/O16, O15/O17, and O15/O16. The Mulliken overlap populations and atomic charges indicate that the metal–oxygen bonding is ionic. The Bravais–Friedel–Donnay–Harker (Bravais, 1866; Friedel, 1907; Donnay & Harker, 1937) morphology is blocky, with {020} as major faces. A 4th-order spherical harmonic model was included in the refinement. The texture index was 1.016, indicating that preferred orientation was slight in the rotated flat-plate specimen.

3. Supramolecular features

The CsO₉ coordination polyhedra share edges and corners to form a three-dimensional framework (Fig. 3). The central hydroxy/carboxylate O–H···O hydrogen O17–H18···O16 is short, and (unusually) intermolecular. The centrosymmetric end-end O12–H20–O12 hydrogen bond (with H20 situated on an inversion center) is exceptionally short and strong (Table 1). By the correlation of Rammohan & Kaduk (2017*a*), these hydrogen bonds contribute 16.5 and 21.7 kcal mol^{−1} to the crystal energy. The hydrophobic methylene groups occupy pockets in the framework (Fig. 3).

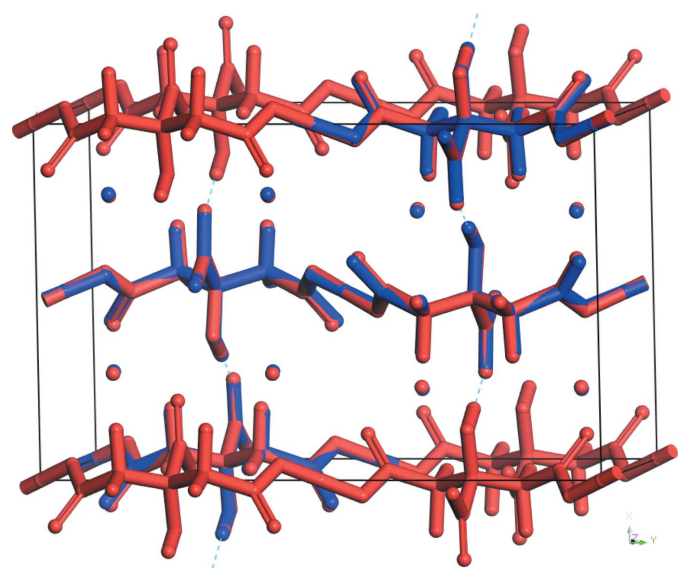


Figure 2
Comparison of the refined and optimized structures of dicesium hydrogen citrate. The refined structure is in red, and the DFT-optimized structure is in blue.

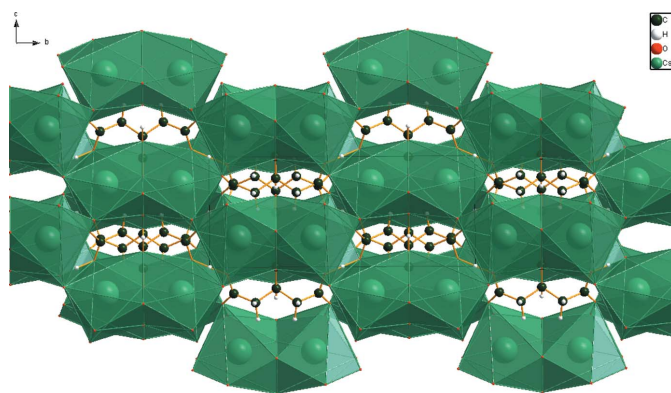


Figure 3
Crystal structure of $\text{Cs}_2\text{HC}_6\text{H}_5\text{O}_7$, viewed down the a -axis. CsO_9 polyhedra are green.

4. Database survey

Details of the comprehensive literature search for citrate structures are presented in Rammohan & Kaduk (2017a). A reduced cell search of the cell of dicesium hydrogen citrate in the Cambridge Structural Database (Groom *et al.*, 2016) (increasing the default tolerance from 1.5 to 2.0%) yielded 100 hits, but combining the cell search with the elements C, H, Cs, and O only yielded no hits.

5. Synthesis and crystallization

Citric acid monohydrate, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$, (2.0796 g, 10.0 mmol) was dissolved in 20 ml deionized water. Cs_2CO_3 (3.2582 g, 10.0 mmol, Sigma–Aldrich) was added to the citric acid solution slowly with stirring. The resulting clear colourless solution was evaporated to dryness in a 333 K oven. Single crystals were isolated from the colourless solid.

6. Refinement

A single crystal was mounted in inert oil and transferred to the cold gas stream of a Bruker Kappa APEX CCD area detector system equipped with a Cu $\text{K}\alpha$ sealed tube with MX optics. Despite suggestions from multiple programs that the space group was $Pnma$, all attempts to refine the structure in this space group yielded unreasonable disorder and non-positive-definite displacement coefficients. Presumably the poor crystal quality and/or twinning were the source of the problems. The best refinement using single crystal data was obtained using space group $P2_12_12_1$.

A portion of the sample was ground in a mortar and pestle, and blended with NIST SRM 640b silicon internal standard. The powder pattern indicated that the sample contained about 24 wt% $\text{CsHC}_6\text{H}_5\text{O}_7$ (Rammohan & Kaduk, 2017f), which was included as phase 2 in the refinement. The Si internal standard was included as phase 3.

Initial Rietveld refinements used the single crystal $P2_12_12_1$ model, but were unstable. The ADDSYM module of PLATON (Spek, 2009) suggested the presence of an addi-

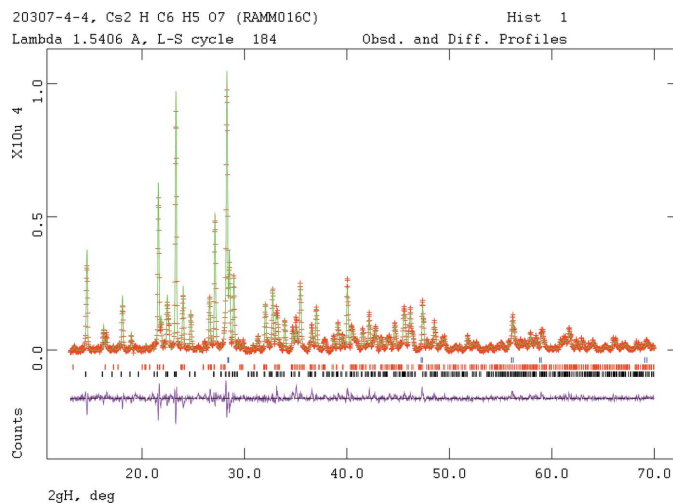


Figure 4
Rietveld plot for the refinement of $\text{Cs}_2\text{HC}_6\text{H}_5\text{O}_7$. The red crosses represent the observed data points, and the green line is the calculated pattern. The magenta curve is the difference pattern, plotted at the same scale as the other patterns. The row of black tick marks indicates the reflection positions, the row of red tick marks indicates the positions of the $\text{Cs}_2\text{HC}_6\text{H}_5\text{O}_7$ impurity peaks, and the blue tick marks indicate the Si internal standard peaks.

tional center of symmetry, and that the correct space group was $Pnma$ (with a transformation of axes). Refinement in the higher-symmetry space group was uneventful. Pseudo-Voigt profile coefficients were as parameterized in Thompson *et al.* (1987) with profile coefficients for Simpson's rule integration of the pseudo-Voigt function according to Howard (1982). The asymmetry correction of Finger *et al.* (1994) was applied, and microstrain broadening by Stephens (1999). The structure was refined by the Rietveld method using *GSAS/EXPGUI* (Larson & Von Dreele, 2004; Toby, 2001). All C–C and C–O bond lengths were restrained, as were all bond angles. The hydrogen atoms were included at fixed positions, which were recalculated during the course of the refinement using *Materials Studio* (Dassault Systemes, 2014). The limited resolution of the powder data precluded refining displacement coefficients, which were fixed at typical values for alkali metal citrates. Diffraction data are displayed in Fig. 4. Crystal data, data collection and structure refinement details are summarized in Table 2.

7. DFT calculations

After the Rietveld refinement, a density functional geometry optimization (fixed experimental unit cell) was carried out using CRYSTAL14 (Dovesi *et al.*, 2014). The basis sets for the C, H, and O atoms were those of Peintinger *et al.* (2012), and the basis set for Cs was that of Sophia *et al.* (2014). The calculation was run on eight 2.1 GHz Xeon cores (each with 6 Gb RAM) of a 304-core Dell Linux cluster at IIT, used 8 k -points and the B3LYP functional, and took about 13 h. The U_{iso} values from the Rietveld refinement were assigned to the optimized fractional coordinates.

Table 2
Experimental details.

	Phase 1	Phase 2
Crystal data		
Chemical formula	$2\text{Cs}^+\cdot\text{C}_6\text{H}_6\text{O}_7^{2-}$	$\text{C}_6\text{H}_7\text{CsO}_7$
M_r	455.92	324.02
Crystal system, space group	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pna2</i> ₁
Temperature (K)	300	300
a, b, c (Å)	9.8466 (3), 15.8872 (5), 6.5959 (2)	8.7362, 20.5351, 5.1682
V (Å ³)	1031.82 (6)	927.17
Z	4	4
Radiation type	$K\alpha_1, K\alpha_2, \lambda = 1.540629, 1.544451 \text{ \AA}$	$K\alpha_1, K\alpha_2, \lambda = 1.540629, 1.544451 \text{ \AA}$
Specimen shape, size (mm)	Flat sheet, 24 × 24	Flat sheet, 24 × 24
Data collection		
Diffractometer	Bruker D2 Phaser	Bruker D2 Phaser
Specimen mounting	Standard PMMA holder	Standard PMMA holder
Data collection mode	Reflection	Reflection
Scan method	Step	Step
2θ values (°)	$2\theta_{\min} = 5.042$ $2\theta_{\max} = 70.050$ $2\theta_{\text{step}} = 0.020$	$2\theta_{\min} = 5.042$ $2\theta_{\max} = 70.050$ $2\theta_{\text{step}} = 0.020$
Refinement		
R factors and goodness of fit	$R_p = 0.050, R_{wp} = 0.062, R_{\text{exp}} = 0.030,$ $R(F^2) = 0.081, \chi^2 = 4.494$	$R_p = 0.050, R_{wp} = 0.062, R_{\text{exp}} = 0.030,$ $R(F^2) = 0.081, \chi^2 = 4.494$
No. of parameters	57	57
No. of restraints	18	18

The same symmetry and lattice parameters were used for the DFT calculation. Computer programs: *DIFFRAC.Measurement* (Bruker, 2009), *SHELXT* (Sheldrick, 2015), *GSAS* (Larson & Von Dreele, 2004), *DIAMOND* (Crystal Impact, 2015), *publCIF* (Westrip, 2010).

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Crystal structure of dicesium hydrogen citrate from laboratory single-crystal and powder X-ray diffraction data and DFT comparison

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Computing details

Data collection: DIFFRAC.Measurement (Bruker, 2009) for RAMM016C_phase_2. Program(s) used to solve structure: SHELXT (Sheldrick, 2015) for RAMM016C_phase_1, RAMM016C_phase_2. Molecular graphics: *DIAMOND* (Crystal Impact, 2015) for RAMM016C_phase_2. Software used to prepare material for publication: *publCIF* (Westrip, 2010) for RAMM016C_phase_2.

(RAMM016C_phase_1) Dicesium hydrogen citrate

Crystal data

$2\text{Cs}^+\cdot\text{C}_6\text{H}_6\text{O}_7^{2-}$	$c = 6.5959 (2) \text{ \AA}$
$M_r = 455.92$	$V = 1031.82 (6) \text{ \AA}^3$
Orthorhombic, <i>Pnma</i>	$Z = 4$
Hall symbol: -P 2ac 2n	$D_x = 2.935 \text{ Mg m}^{-3}$
$a = 9.8466 (3) \text{ \AA}$	$T = 300 \text{ K}$
$b = 15.8872 (5) \text{ \AA}$	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.485 (3)	0.4027 (17)	0.728 (4)	0.03*
C2	0.536 (3)	0.3251 (14)	0.837 (3)	0.03*
C3	0.503 (4)	0.25	0.697 (5)	0.03*
C6	0.595 (3)	0.25	0.507 (4)	0.03*
H7	0.4982	0.8239	0.0123	0.039*
H8	0.3388	0.8299	0.1638	0.039*
O11	0.389 (2)	0.4449 (13)	0.807 (4)	0.03*
O12	0.549 (3)	0.4350 (14)	0.580 (3)	0.03*
O15	0.529 (3)	0.25	0.340 (4)	0.03*
O16	0.724 (3)	0.25	0.524 (4)	0.03*
O17	0.367 (4)	0.25	0.627 (4)	0.03*
H18	0.3147	0.25	0.748	0.039*
Cs19	0.28419 (18)	0.39202 (15)	0.2547 (10)	0.02*
H20	0.5	0.5	0.5	0.039*

Geometric parameters (Å, °)

C1—C2	1.510 (2)	O12—H20	1.25 (2)
C1—O11	1.270 (2)	O15—C6	1.275 (6)
C1—O12	1.273 (6)	O15—Cs19	3.35 (2)
C2—C1	1.510 (2)	O15—Cs19 ⁱⁱ	3.35 (2)
C2—C3	1.540 (2)	O15—Cs19 ^{viii}	3.43 (2)
C2—H7 ⁱ	1.05 (3)	O15—Cs19 ^{vii}	3.43 (2)
C2—H8 ⁱ	1.23 (3)	O16—C6	1.273 (6)
C3—C2	1.540 (2)	O16—Cs19 ^{viii}	2.971 (18)
C3—C2 ⁱⁱ	1.540 (2)	O16—Cs19 ^{vii}	2.971 (18)
C3—C6	1.550 (2)	O17—C3	1.421 (6)
C3—O17	1.421 (6)	O17—H18	0.95 (3)
C6—C3	1.550 (2)	O17—Cs19	3.43 (2)
C6—O15	1.275 (6)	O17—Cs19 ⁱⁱ	3.43 (2)
C6—O16	1.273 (6)	H18—O17	0.95 (3)
H7—C2 ⁱⁱⁱ	1.05 (3)	Cs19—O11 ^{ix}	3.24 (2)
H8—C2 ⁱⁱⁱ	1.23 (3)	Cs19—O11	3.88 (2)
O11—C1	1.270 (2)	Cs19—O11 ^x	3.12 (2)
O11—Cs19	3.88 (2)	Cs19—O12	3.44 (3)
O11—Cs19 ^{iv}	3.24 (2)	Cs19—O12 ^{vi}	3.38 (3)
O11—Cs19 ^v	3.12 (2)	Cs19—O12 ^{xi}	3.27 (2)
O12—C1	1.273 (6)	Cs19—O15	3.35 (2)
O12—Cs19	3.44 (3)	Cs19—O15 ^{xii}	3.43 (2)
O12—Cs19 ^{vi}	3.38 (3)	Cs19—O16 ^{xii}	2.971 (18)
O12—Cs19 ^{vii}	3.27 (2)	Cs19—O17	3.43 (2)
C2—C1—O11	119 (2)	Cs19—O17—Cs19 ⁱⁱ	82.2 (6)
C2—C1—O12	122 (2)	O11 ^{ix} —Cs19—O11 ^x	93.4 (5)
O11—C1—O12	118 (3)	O11 ^{ix} —Cs19—O12	106.0 (6)
C1—C2—C3	106.4 (17)	O11 ^{ix} —Cs19—O12 ^{vi}	85.9 (5)
C1—C2—H7 ⁱⁱⁱ	111 (2)	O11 ^{ix} —Cs19—O12 ^{xv}	63.7 (6)
C1—C2—H8 ⁱⁱⁱ	106 (2)	O11 ^{ix} —Cs19—O15	95.7 (6)
C3—C2—H7 ⁱⁱⁱ	119 (3)	O11 ^{ix} —Cs19—O15 ^{xvi}	103.7 (6)
C3—C2—H8 ⁱⁱⁱ	105 (2)	O11 ^{ix} —Cs19—O16 ^{xvi}	72.3 (6)
H7 ⁱⁱⁱ —C2—H8 ⁱⁱⁱ	108.8 (18)	O11 ^{ix} —Cs19—O17	138.4 (6)
C2—C3—C2 ⁱⁱ	102 (3)	O11 ^x —Cs19—O12	100.4 (6)
C2—C3—C6	111.1 (18)	O11 ^x —Cs19—O12 ^{vi}	63.6 (6)
C2—C3—O17	113 (2)	O11 ^x —Cs19—O12 ^{xv}	60.9 (6)
C2 ⁱⁱ —C3—C6	111.1 (18)	O11 ^x —Cs19—O15	159.0 (5)
C2 ⁱⁱ —C3—O17	113 (2)	O11 ^x —Cs19—O15 ^{xvi}	99.6 (5)
C6—C3—O17	107 (2)	O11 ^x —Cs19—O16 ^{xvi}	126.1 (6)
C3—C6—O15	114 (3)	O11 ^x —Cs19—O17	126.6 (6)
C3—C6—O16	121 (3)	O12—Cs19—O12 ^{vi}	43.1 (7)
C1—O11—Cs19 ^{iv}	118.2 (17)	O12—Cs19—O12 ^{xv}	156.1 (7)
C1—O11—Cs19 ^v	143.2 (19)	O12—Cs19—O15	58.9 (5)
Cs19 ^{iv} —O11—Cs19 ^v	98.2 (7)	O12—Cs19—O15 ^{xvi}	142.9 (5)
C1—O12—Cs19	92 (3)	O12—Cs19—O16 ^{xvi}	133.4 (7)

C1—O12—Cs19 ^{vi}	109 (2)	O12—Cs19—O17	60.4 (5)
C1—O12—Cs19 ^{xiii}	141.7 (17)	O12 ^{vi} —Cs19—O12 ^{xv}	113.1 (5)
Cs19—O12—Cs19 ^{vi}	136.9 (7)	O12 ^{vi} —Cs19—O15	98.2 (5)
Cs19—O12—Cs19 ^{xiii}	94.3 (6)	O12 ^{vi} —Cs19—O15 ^{xvi}	161.4 (5)
C6—O15—Cs19	120.8 (14)	O12 ^{vi} —Cs19—O16 ^{xvi}	156.0 (7)
C6—O15—Cs19 ⁱⁱ	120.8 (14)	O12 ^{vi} —Cs19—O17	100.8 (6)
C6—O15—Cs19 ^{xiv}	77.5 (15)	O12 ^{xv} —Cs19—O15	139.8 (6)
C6—O15—Cs19 ^{xiii}	77.5 (15)	O12 ^{xv} —Cs19—O15 ^{xvi}	59.7 (6)
Cs19—O15—Cs19 ⁱⁱ	84.7 (7)	O12 ^{xv} —Cs19—O16 ^{xvi}	66.4 (6)
Cs19—O15—Cs19 ^{xiv}	159.7 (9)	O12 ^{xv} —Cs19—O17	141.9 (7)
Cs19—O15—Cs19 ^{xiii}	93.05 (18)	O15—Cs19—O15 ^{xvi}	96.59 (14)
Cs19 ⁱⁱ —O15—Cs19 ^{xiv}	93.05 (18)	O15—Cs19—O16 ^{xvi}	74.7 (5)
Cs19 ⁱⁱ —O15—Cs19 ^{xiii}	159.7 (9)	O15—Cs19—O17	42.8 (7)
Cs19 ^{xiv} —O15—Cs19 ^{xiii}	82.1 (6)	O15 ^{xvi} —Cs19—O16 ^{xvi}	40.7 (6)
C6—O16—Cs19 ^{xiv}	98.2 (15)	O15 ^{xvi} —Cs19—O17	82.6 (7)
C6—O16—Cs19 ^{xiii}	98.2 (15)	O16 ^{xvi} —Cs19—O17	89.5 (5)
Cs19 ^{xiv} —O16—Cs19 ^{xiii}	98.8 (8)	O12—H20—O12 ^{vi}	180.0

Symmetry codes: (i) $-x+1, y-1/2, -z+1$; (ii) $x, -y+1/2, z$; (iii) $-x+1, y+1/2, -z+1$; (iv) $x, y, z+1$; (v) $-x+1/2, -y+1, z+1/2$; (vi) $-x+1, -y+1, -z+1$; (vii) $x+1/2, y, -z+1/2$; (viii) $x+1/2, -y+1/2, -z+1/2$; (ix) $x, y, z-1$; (x) $-x+1/2, -y+1, z-1/2$; (xi) $x-1/2, y, -z+1/2$; (xii) $x-1/2, -y+1/2, -z+1/2$; (xiii) $x+3/2, y, -z+3/2$; (xiv) $x+3/2, -y+3/2, -z+3/2$; (xv) $x+1/2, y, -z+3/2$; (xvi) $x+1/2, -y+3/2, -z+3/2$.

(RAMM016C_phase_2) cesium dihydrogen citrate

Crystal data

$C_6H_7CsO_7$

$M_r = 324.02$

Orthorhombic, $Pna2_1$

Hall symbol: $P\ 2c\ -2n$

$a = 8.7362\ \text{\AA}$

$b = 20.5351\ \text{\AA}$

$c = 5.1682\ \text{\AA}$

$V = 927.17\ \text{\AA}^3$

$Z = 4$

$D_x = 2.321\ \text{Mg m}^{-3}$

$T = 300\ \text{K}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1877	0.0459	0.281	0.065*
C2	0.3465	0.0446	0.166	0.009*
C3	0.4423	0.0965	0.304	0.009*
C4	0.6089	0.0896	0.212	0.009*
C5	0.7062	0.1464	0.317	0.065*
C6	0.3805	0.1664	0.241	0.065*
O7	0.1302	-0.0065	0.333	0.065*
O8	0.1066	0.0875	0.223	0.065*
O9	0.371	0.1861	0.009	0.065*
O10	0.351	0.2038	0.417	0.065*
O11	0.7164	0.1977	0.185	0.065*
O12	0.7293	0.1503	0.553	0.065*
O13	0.4359	0.0847	0.577	0.065*
H14	0.4007	-0.0062	0.1958	0.012*
H15	0.3339	0.0538	-0.0498	0.012*
H16	0.4251	0.132	0.7041	0.085*

H17	0.6502	0.0404	0.2549	0.012*
H18	0.6012	0.0942	-0.0229	0.012*
Cs19	0.04535	0.20017	0.7594	0.0503*
H20	0.0694	-0.0507	0.5686	0.039*
H21	0.67528	0.243	0.2524	0.039*

Geometric parameters (Å, °)

C1—C2	1.5095	O12—C5	1.2389
C1—O7	1.2176	O12—O11	2.1395
C1—O8	1.1496	O12—Cs19 ⁱ	3.1321
C2—C1	1.5095	O12—Cs19 ^v	3.6262
C2—C3	1.5313	O13—C3	1.4327
C2—H14	1.1559	O13—H16	1.1764
C2—H15	1.1365	H14—C2	1.1559
C3—C2	1.5313	H14—H15	1.8627
C3—C4	1.5377	H15—C2	1.1365
C3—C6	1.5678	H15—H14	1.8627
C3—O13	1.4327	H16—O9 ^{viii}	1.9851
C4—C3	1.5377	H16—O13	1.1764
C4—C5	1.5419	H16—Cs19	3.6122
C4—H17	1.0955	H16—Cs19 ^v	3.6143
C4—H18	1.2195	H17—C4	1.0955
C5—C4	1.5419	H17—H18	1.8615
C5—O11	1.2582	H18—C4	1.2195
C5—O12	1.2389	H18—H17	1.8615
C5—Cs19 ⁱ	3.9020	Cs19—C5 ^{ix}	3.9020
C5—H21	2.0297	Cs19—C6	4.0289
C6—C3	1.5678	Cs19—C6 ^{viii}	3.9050
C6—O9	1.2682	Cs19—C6 ^x	3.972
C6—O10	1.2181	Cs19—O8	3.6503
C6—Cs19 ⁱⁱ	3.9050	Cs19—O8 ^{viii}	3.3735
C6—Cs19	4.0289	Cs19—O9 ^{viii}	3.1371
C6—Cs19 ⁱⁱⁱ	3.972	Cs19—O9 ^x	3.0722
O7—C1	1.2176	Cs19—O10	3.2042
O7—O8	2.0228	Cs19—O10 ^{vi}	3.1469
O7—H20	1.6089	Cs19—O11 ^{xi}	3.6193
O8—C1	1.1496	Cs19—O11 ^{vi}	3.9299
O8—O7	2.0228	Cs19—O11 ^x	3.3867
O8—Cs19 ⁱⁱ	3.3735	Cs19—O12 ^{ix}	3.1321
O8—Cs19	3.6503	Cs19—O12 ^{vi}	3.6262
O8—H20 ^{iv}	1.8900	Cs19—H16	3.6122
O9—C6	1.2682	Cs19—H16 ^{vi}	3.6143
O9—O10	2.1468	Cs19—Cs19 ⁱⁱ	5.1682
O9—H16 ⁱⁱ	1.9851	Cs19—Cs19 ^{viii}	5.1682
O9—Cs19 ⁱⁱ	3.1371	Cs19—Cs19 ^{vi}	4.8238
O9—Cs19 ⁱⁱⁱ	3.0722	Cs19—Cs19 ^v	4.8238
O10—C6	1.2181	Cs19—H20 ^{xii}	3.6027

O10—O9	2.1468	Cs19—H21 ^{vi}	3.0848
O10—Cs19	3.2042	Cs19—H21 ^x	3.0236
O10—Cs19 ^v	3.1469	H20—O7	1.6089
O10—H21 ^{vi}	2.0673	H20—O8 ^{xii}	1.8900
O11—C5	1.2582	H20—Cs19 ^{iv}	3.6027
O11—O12	2.1395	H21—C5	2.0297
O11—Cs19 ^{vii}	3.6193	H21—O10 ^v	2.0673
O11—Cs19 ⁱⁱⁱ	3.3867	H21—O11	1.0563
O11—Cs19 ^v	3.9299	H21—Cs19 ⁱⁱⁱ	3.0236
O11—H21	1.0563	H21—Cs19 ^v	3.0848
C2—C1—O7	116.7731	O9 ^x —Cs19—O10 ^{vi}	59.4859
C2—C1—O8	118.4826	O9 ^x —Cs19—O11 ^{xi}	50.343
O7—C1—O8	117.3875	O9 ^x —Cs19—O11 ^x	58.3514
C1—C2—C3	107.8548	O9 ^x —Cs19—O12 ^{ix}	87.3923
C1—C2—H14	109.8752	O9 ^x —Cs19—Cs19 ⁱⁱ	114.8276
C1—C2—H15	107.1232	O9 ^x —Cs19—Cs19 ^{viii}	65.1724
C3—C2—H14	110.0087	O9 ^x —Cs19—Cs19 ^{vi}	39.5136
C3—C2—H15	113.2215	O9 ^x —Cs19—Cs19 ^v	97.2637
H14—C2—H15	108.6894	O9 ^x —Cs19—H21 ^{vi}	104.5664
C2—C3—C4	108.0085	O9 ^x —Cs19—H21 ^x	62.5411
C2—C3—C6	110.6267	O10—Cs19—O10 ^{vi}	97.1512
C2—C3—O13	108.6407	O10—Cs19—O11 ^{xi}	176.0673
C4—C3—C6	110.2492	O10—Cs19—O11 ^x	88.658
C4—C3—O13	109.0185	O10—Cs19—O12 ^{ix}	123.6515
C6—C3—O13	110.2395	O10—Cs19—Cs19 ⁱⁱ	56.4773
C3—C4—C5	110.0762	O10—Cs19—Cs19 ^{viii}	123.5227
C3—C4—H17	109.5203	O10—Cs19—Cs19 ^{vi}	138.138
C3—C4—H18	104.3867	O10—Cs19—Cs19 ^v	40.1379
C5—C4—H17	116.414	O10—Cs19—H21 ^{vi}	38.3222
C5—C4—H18	108.7936	O10—Cs19—H21 ^x	98.2538
H17—C4—H18	106.9223	O10 ^{vi} —Cs19—O11 ^{xi}	85.5337
C4—C5—O11	118.7882	O10 ^{vi} —Cs19—O11 ^x	102.4289
C4—C5—O12	119.0252	O10 ^{vi} —Cs19—O12 ^{ix}	62.4676
O11—C5—O12	117.9141	O10 ^{vi} —Cs19—Cs19 ⁱⁱ	55.783
C3—C6—O9	120.7284	O10 ^{vi} —Cs19—Cs19 ^{viii}	124.217
C3—C6—O10	119.6742	O10 ^{vi} —Cs19—Cs19 ^{vi}	41.0239
O9—C6—O10	119.4116	O10 ^{vi} —Cs19—Cs19 ^v	102.8686
C1—O7—H20	143.3052	O10 ^{vi} —Cs19—H21 ^{vi}	58.9237
C1—O8—Cs19 ⁱⁱ	142.4291	O10 ^{vi} —Cs19—H21 ^x	115.7564
C6—O9—Cs19 ⁱⁱ	118.5237	O11 ^{xi} —Cs19—O11 ^x	87.9548
C6—O9—Cs19 ⁱⁱⁱ	127.377	O11 ^{xi} —Cs19—O12 ^{ix}	60.1617
Cs19 ⁱⁱ —O9—Cs19 ⁱⁱⁱ	101.9433	O11 ^{xi} —Cs19—Cs19 ⁱⁱ	127.4261
C6—O10—Cs19	125.0345	O11 ^{xi} —Cs19—Cs19 ^{viii}	52.5739
C6—O10—Cs19 ^v	134.4984	O11 ^{xi} —Cs19—Cs19 ^{vi}	44.5151
Cs19—O10—Cs19 ^v	98.8382	O11 ^{xi} —Cs19—Cs19 ^v	136.4653
C5—O11—Cs19 ^{vii}	113.4209	O11 ^{xi} —Cs19—H21 ^{vi}	144.4574
C5—O11—Cs19 ⁱⁱⁱ	147.075	O11 ^{xi} —Cs19—H21 ^x	77.9576

C5—O11—H21	122.3074	O11 ^x —Cs19—O12 ^{ix}	144.3543
Cs19 ^{vii} —O11—Cs19 ⁱⁱⁱ	86.9593	O11 ^x —Cs19—Cs19 ⁱⁱ	130.5024
Cs19 ^{vii} —O11—H21	117.2654	O11 ^x —Cs19—Cs19 ^{viii}	49.4976
Cs19 ⁱⁱⁱ —O11—H21	61.2332	O11 ^x —Cs19—Cs19 ^{vi}	97.8643
C5—O12—Cs19 ⁱ	120.0024	O11 ^x —Cs19—Cs19 ^v	48.5256
C3—O13—H16	114.4184	O11 ^x —Cs19—H21 ^{vi}	98.9194
O8 ^{viii} —Cs19—O9 ^{viii}	60.0614	O11 ^x —Cs19—H21 ^x	17.8322
O8 ^{viii} —Cs19—O9 ^x	107.5655	O12 ^{ix} —Cs19—Cs19 ⁱⁱ	70.0882
O8 ^{viii} —Cs19—O10	106.0226	O12 ^{ix} —Cs19—Cs19 ^{viii}	109.9118
O8 ^{viii} —Cs19—O10 ^{vi}	156.1712	O12 ^{ix} —Cs19—Cs19 ^{vi}	48.7345
O8 ^{viii} —Cs19—O11 ^{xi}	71.6205	O12 ^{ix} —Cs19—Cs19 ^v	159.551
O8 ^{viii} —Cs19—O11 ^x	83.8832	O12 ^{ix} —Cs19—H21 ^{vi}	99.1359
O8 ^{viii} —Cs19—O12 ^{ix}	99.0601	O12 ^{ix} —Cs19—H21 ^x	138.084
O8 ^{viii} —Cs19—Cs19 ⁱⁱ	135.2548	Cs19 ⁱⁱ —Cs19—Cs19 ^{viii}	180.0
O8 ^{viii} —Cs19—Cs19 ^{viii}	44.7452	Cs19 ⁱⁱ —Cs19—Cs19 ^{vi}	90.0
O8 ^{viii} —Cs19—Cs19 ^{vi}	115.7608	Cs19 ⁱⁱ —Cs19—Cs19 ^v	90.0
O8 ^{viii} —Cs19—Cs19 ^v	98.4731	Cs19 ⁱⁱ —Cs19—H21 ^{vi}	31.8529
O8 ^{viii} —Cs19—H21 ^{vi}	143.5507	Cs19 ⁱⁱ —Cs19—H21 ^x	147.4235
O8 ^{viii} —Cs19—H21 ^x	66.8377	Cs19 ^{viii} —Cs19—Cs19 ^{vi}	90.0
O9 ^{viii} —Cs19—O9 ^x	110.3022	Cs19 ^{viii} —Cs19—Cs19 ^v	90.0
O9 ^{viii} —Cs19—O10	58.2306	Cs19 ^{viii} —Cs19—H21 ^{vi}	148.1471
O9 ^{viii} —Cs19—O10 ^{vi}	141.1001	Cs19 ^{viii} —Cs19—H21 ^x	32.5765
O9 ^{viii} —Cs19—O11 ^{xi}	117.9614	Cs19 ^{vi} —Cs19—Cs19 ^v	129.7922
O9 ^{viii} —Cs19—O11 ^x	52.3974	Cs19 ^{vi} —Cs19—H21 ^{vi}	99.9449
O9 ^{viii} —Cs19—O12 ^{ix}	155.4194	Cs19 ^{vi} —Cs19—H21 ^x	100.1484
O9 ^{viii} —Cs19—Cs19 ⁱⁱ	114.2806	Cs19 ^v —Cs19—H21 ^{vi}	60.4158
O9 ^{viii} —Cs19—Cs19 ^{viii}	65.7194	Cs19 ^v —Cs19—H21 ^x	59.755
O9 ^{viii} —Cs19—Cs19 ^{vi}	149.3491	H21 ^{vi} —Cs19—H21 ^x	115.5707
O9 ^{viii} —Cs19—Cs19 ^v	38.5431	O11—H21—Cs19 ⁱⁱⁱ	100.9346
O9 ^{viii} —Cs19—H21 ^{vi}	92.8906	O11—H21—Cs19 ^v	137.5968
O9 ^{viii} —Cs19—H21 ^x	49.3517	Cs19 ⁱⁱⁱ —H21—Cs19 ^v	115.5707
O9 ^x —Cs19—O10	128.8561		

Symmetry codes: (i) $x+1, y, z$; (ii) $x, y, z-1$; (iii) $x+1/2, -y+1/2, z-1$; (iv) $-x, -y, z-1/2$; (v) $x+1/2, -y+1/2, z$; (vi) $x-1/2, -y+1/2, z$; (vii) $x+1, y, z-1$; (viii) $x, y, z+1$; (ix) $x-1, y, z$; (x) $x-1/2, -y+1/2, z+1$; (xi) $x-1, y, z+1$; (xii) $-x, -y, z+1/2$.

(RAMM016C_phase_3) silicon

Crystal data

Si
 $M_r = 28.09$
 Cubic, $Fd\bar{3}m$
 Hall symbol: -F 4vw 2vw
 $a = 5.43105 \text{ \AA}$

$V = 160.20 \text{ \AA}^3$
 $Z = 8$
 $D_x = 2.329 \text{ Mg m}^{-3}$
 $T = 300 \text{ K}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Si1	0.125	0.125	0.125	0.01*

Geometric parameters (\AA , $^\circ$)

Si1—Si1 ⁱ	2.3517	Si1—Si1 ⁱⁱⁱ	2.3517
Si1—Si1 ⁱⁱ	2.3517	Si1—Si1 ^{iv}	2.3517
Si1 ⁱ —Si1—Si1 ⁱⁱ	109.4712	Si1 ⁱⁱ —Si1—Si1 ⁱⁱⁱ	109.4712
Si1 ⁱ —Si1—Si1 ⁱⁱⁱ	109.4712	Si1 ⁱⁱ —Si1—Si1 ^{iv}	109.4712
Si1 ⁱ —Si1—Si1 ^{iv}	109.4712	Si1 ⁱⁱⁱ —Si1—Si1 ^{iv}	109.4712

Symmetry codes: (i) $x+1/4, y+1/4, -z$; (ii) $-z, x+1/4, y+1/4$; (iii) $y+1/4, -z, x+1/4$; (iv) $-x, -y, -z$.

(ramm016c_DFT)

Crystal data

$\text{C}_6\text{H}_6\text{Cs}_2\text{O}_7$	$b = 15.8872 \text{ \AA}$
$M_r = 455.92$	$c = 6.5959 \text{ \AA}$
Orthorhombic, <i>Pnma</i>	$V = 1031.82 \text{ \AA}^3$
Hall symbol: $-P\ 2ac\ 2n$	$Z = 4$
$a = 9.8466 \text{ \AA}$	$T = 300 \text{ K}$

Data collection

$h = \rightarrow$	$l = \rightarrow$
$k = \rightarrow$	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.48590	0.40995	0.73839	0.03000*
C2	0.53924	0.32807	0.82202	0.03000*
H7	0.49922	0.81932	0.02513	0.03900*
H8	0.35061	0.83203	0.17117	0.03900*
O11	0.39754	0.45079	0.82841	0.03000*
O12	0.54129	0.43424	0.56822	0.03000*
Cs19	0.28894	0.39193	0.26540	0.02000*
C3	0.50141	0.25000	0.69412	0.03000*
C6	0.58468	0.25000	0.49542	0.03000*
O15	0.52651	0.25000	0.32675	0.03000*
O16	0.71279	0.25000	0.52034	0.03000*
O17	0.36003	0.25000	0.64658	0.03000*
H18	0.30582	0.25000	0.77454	0.03900*
H20	0.50000	0.50000	0.50000	0.03900*

Bond lengths (\AA)

C1—C2	1.507	O12—H20	1.208
C1—O11	1.237	C3—C2 ⁱⁱⁱ	1.546
C1—O12	1.306	C3—C6	1.546
C2—C3	1.546	C3—O17	1.427
C2—H7 ⁱ	1.086	C6—O15	1.251
C2—H8 ⁱ	1.087	C6—O16	1.272

H7—C2 ⁱⁱ	1.086	O17—H18	0.999
H8—C2 ⁱⁱ	1.087	H20—O12 ^{iv}	1.208

Symmetry codes: (i) $-x+1, y-1/2, -z+1$; (ii) $-x+1, y+1/2, -z+1$; (iii) $x, -y+1/2, z$; (iv) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O12—H20...O12 ^{iv}	1.208	1.208	2.416	180.0
O17—H18...O16 ^v	0.999	1.634	2.632	178.2

Symmetry codes: (iv) $-x+1, -y+1, -z+1$; (v) $x-1/2, -y+1/2, -z+3/2$.